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(54) Catalyst for the hydroisomerization of long-chain N-paraffins and process for preparing it

Katalysator zur Hydroisomerisierung von langkettigen N-Paraffinen und Verfahren zu seiner
Herstellung

Catalyseur d'hydroisomérisation de N-paraffines à longue chaîne et procédé de sa préparation

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EP-A- 0 225 053 EP-A- 0 340 868
US-A- 3 637 484 US-A- 3 657 153
US-A- 3 855 347

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Description

The present invention relates to a bifunctional catalyst constituted by a calcined amorphous silica and alumina gel, and one or more noble metals belonging to Group VIIIA, to the preparation of such a catalyst and to its use in hydroisomerization of long-chain n-paraffins containing more than 15 carbon atoms.

The process of wax isomerization to yield lubricant oil bases characterized by a low pour point and by a high viscosity index, requires the use of suitable catalysts.

In fact, the waxes, mainly constituted (>80% by weight) by n-paraffins containing more than 15 carbon atoms and solid at room temperature, must be converted into their corresponding branched isomers having a higher melting point than their linear isomers.

For example, the n-C₁₆ paraffin has a melting point of 19°C, whilst its 5-methyl pentadecane isomer melts at -31°C.

An effective hydroisomerization catalyst should anyway minimize the possible cracking and hydrocracking reactions, which are catalyzed by the same acidic sites, and have, as intermediates, the same carbocations useful for hydroisomerization. These side reactions cause the degradation of the molecule, with less valuable, lighter products being formed, which must be removed from the end product in order not to increase the volatility thereof; the need for such additional removal step obviously increases the general costs of the overall process.

For this process, bifunctional catalysts were developed, i.e., catalysts which are provided with both acidic sites and hydro-dehydrogenation active sites. The acidity is given to the catalyst by the type of selected carrier, and its function exactly is supplying the catalysts with such an isomerizing property.

The hydro-dehydrogenation activity is supplied to the catalyst by the deposited metal phase, the function of which is also of keeping cracking reactions to a very minimum.

It was demonstrated (J. F. Le Page, *Applied Heterogeneous Catalysis*, Ed. Technip, Paris, 1987, 435-466) that, with the hydrogenating activity being the same, the more selective catalysts are those in which the carrier has a controlled acidity, so as to maximize the isomerization of n-paraffins, over cracking reactions. However, inasmuch as the cracking reactions take place after the isomerization reactions, the maximal isomerization selectivity is obtained at low conversion levels (G. Froment et al., *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, 20, 654-660).

The effectiveness of various catalysts can be evaluated on model compounds as n-paraffins, by measuring the selectivity thereof, i.e., the ratio of the isomerization products to the cracking products, at a given level of conversion of n-paraffins.

Among most recent patents, EP-A-321,307 discloses a process for wax hydroisomerization in order to produce lubricant oil bases, which implies a hydroisomerization step carried out in the presence of a particular catalyst. The latter contains from 0.1 to 5% by weight of a metal belonging to Group VI or VIIIA, preferably VIIIA, still more preferably a noble metal of Group VIIIA, in the most preferred form, platinum supported on a halogenated, preferably fluorinated, refractory inorganic oxide.

The halogenation of the inorganic oxide is known to increase the acidity thereof. In particular, the surface acidity of fluorinated aluminas and their catalytic activity in the reactions occurring via carbocation, is a function of their fluorine content (R. Covini, V. Fattore, N. Giordano, *J. Catal.*, 1967, 9, 315-321).

EP-A-225 053 discloses a further process for hydroisomerizing waxes, in which provided is a hydroisomerization step carried out in the presence of a catalyst constituted by beta zeolite plus one effective component in hydrogenation-dehydrogenation reaction, preferably a noble metal. This catalyst has a high SiO₂:Al₂O₃ ratio, at least equal to 30, preferably higher than 50, for example comprised within the range of from 100 to 500, in order to reduce the acidity thereof and consequently the possible cracking reactions.

As regards the process, both the above cited patents report that wax conversions should be limited to 20-40% by weight, in order to minimize the formation of light products caused by cracking.

The catalyst disclosed in EP-A-321,307 suffers from the drawback that it should be prepared by starting from a highly toxic and corrosive reactant as HF, dissolved in water together with NH₄F.

US-A-3,657,153 discloses a process for preparing a silica/alumina supported noble metal catalyst by impregnating the carrier with a solution of hexachloroplatinic acid. Such catalyst presents a high alumina content with respect to the silica content. US-A-3,855,347 concerns a catalyst of hydrogenation of halogenated hydrocarbons, consisting of a metal of Group VIIIA deposited on silica/alumina, having only a supporting function.

Also US-A-3,637,484 discloses a process for preparing a silica/alumina supported noble metal catalyst. This support of silica/alumina cogel presents a high acidity.

The process disclosed in EP-A-225 053 uses a catalyst in which the beta zeolite is prepared according to as disclosed in US-A-3,308,069, US-A-4,419,220 and US-A-4,518,485. Owing to the low ratio of SiO₂:Al₂O₃, typical of this beta zeolite, a dealumination should be carried out by steaming and/or acidic treatment of the starting zeolite in order to obtain acceptable selectivity values. In fact, owing to the high acidity of zeolites, under the hydroisomerization conditions the cracking reaction is very competitive with the isomerization reaction. The de-alumination requires the addition of a further step in the global catalyst synthesis which, with the crystallization being performed under hydrothermal conditions, is, per se, already much more complex than the preparation of an amorphous silica-alumina.

In EP-A-340 868, disclosed is an amorphous and microporous silica-alumina gel, active in the processes of isomerization, alkylation, dewaxing and dimerization of linear olefins. Typical characteristics of said material are its high acidity, as compared to conventional amorphous silica-aluminas and the very narrow distribution of its average pore diameter.

The present Applicant found now, according to the present invention, that using a gel of the same type as disclosed in EP-A-340 868 as the acidic carrier for limited amounts of metals of Group VIIIA, in particular palladium and platinum, makes it possible a catalyst to be obtained with uniform and controlled porosity, which is effective in paraffin hydroisomerization, also without any treatments with fluorinated compounds.

In accordance therewith, the present invention relates to a bifunctional catalyst for the hydroisomerization of n-paraffins containing more than 15 carbon atoms constituted by:

- (a) a carrier of acidic character constituted by a calcined X-ray amorphous silica and alumina gel, with a molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ comprised within the range of from 30:1 to 500:1, a surface area comprised within the range of from 500 to 1000 m^2/g , with a porosity comprised within the range of from 0.3 to 0.6 ml/g , with an average diameter of pores comprised within the range of from 10 to $30 \cdot 10^{-10}$ m (10 to 30 Angstroms);
- (b) one or more noble metals belonging to Group VIIIA, in amounts comprised within the range of from 0.05 to 5% by weight.

In the preferred embodiment, the acidic carrier of the present invention displays a ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ comprised within the range of from 50:1 to 300:1 and a porosity of the order of 0.4-0.5 ml/g , and the noble metal, selected from platinum and palladium, is contained at a level of from 0.1 to 2% by weight.

The present invention relates also to a process for preparing the above mentioned bifunctional catalyst according to claims 4-7, and to a process for hydromerizing n-paraffin according to claims 8-10.

The silica and alumina gel can be advantageously prepared according to as disclosed in EP-A-340 868; in particular, an aqueous solution of a tetra alkyl ammonium hydroxide (TAA-OH), is prepared, in which "alkyl" means ethyl, n-propyl or n-butyl, of a soluble aluminum compound capable of yielding Al_2O_3 by hydrolysis, and a soluble silicon compound capable of yielding SiO_2 by hydrolysis, with the amount of said constituents in said solution being such that the following molar ratios are complied with:

- * $\text{SiO}_2:\text{Al}_2\text{O}_3$ from 30:1 to 500:1;
- * TAA-OH: SiO_2 from 0.05:1 to 0.2:1;
- * $\text{H}_2\text{O}:\text{SiO}_2$ from 5:1 to 40:1;

and the resulting solution is heated in order to cause it to undergo gelation; the resulting gel is dried and is calcined under an inert atmosphere and then under an oxidizing atmosphere.

The metal phase can be added either by impregnation from an aqueous medium, or by ionic exchange.

More particularly, according to the first operating technique, the silica-alumina gel, prepared as disclosed above, is wetted with an aqueous solution of a compound of the selected noble metal, for example chloroplatinic acid or $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$, by operating at room or close-to-room temperatures, and at a pH value of the order of 1-4 pH units. After aqueous impregnation, the solid material is dried, preferably in air, at room or close-to-room temperatures, and is submitted to a thermal treatment under an oxidizing atmosphere, preferably in air. Suitable temperatures for this thermal treatment are comprised within the range of from 200 to 600°C. The conditions are so adjusted that on silica-alumina particles an amount of noble metal is deposited which is comprised within the range of from 0.05 to 5% by weight, preferably of from 0.1 to 2%.

According to the operating technique based on ionic exchange, the silica-alumina gel is suspended in an aqueous solution of a noble metal complex or salt, for example, an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ or of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ or of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$, by operating at room or close-to-room temperatures, and at a pH value comprised within the range of from 6 to 10. After the ionic exchange the solid matter is separated, then is washed with water, is dried and finally is submitted to thermal treatment in an inert or oxidizing atmosphere. Thermal treatment temperatures comprised within the range of from 200 to 600°C were found useful. The conditions are so controlled, that an amount of noble metal comprised within the range of from 0.05 to 5% by weight, preferably of from 0.1 to 2%, is deposited on silica-alumina particles.

In any cases, after these ionic exchange or aqueous impregnation operations, bifunctional catalysts are obtained which consist of silica-alumina gel carriers loaded with a noble metal, having in general a surface area comprised within the range of from 300 to 900 m^2/g .

The best results in terms of catalytic activity in the hydroisomerization process are obtained with the catalysts prepared according to the technique of aqueous impregnation, which display high values of paraffin conversion, together with good results of selectivity to isoparaffins.

In the case when one wishes to operate at low paraffin conversion rates, those catalysts are however preferable which are prepared by means of the ionic exchange technique, and, among these, preferably those which contain palladium which, at low conversion rates, display very good selectivities to isoparaffins.

The catalysts according to the present invention can be activated by drying and/or reduction, preferably by drying and subsequent reduction. The drying is carried out in an inert atmosphere at a temperature comprised within the range of from 100 to 400°C, and the reduction is obtained by means of the thermal treatment of the sample under a reducing atmosphere at temperatures comprised within the range of from 150 to 500°C. These steps, which constitute additional steps to the whole process, result to be essential in order to obtain the desired improvement in the performance of the same catalysts, because they increase the selectivity characteristics thereof.

The catalysts according to the present invention can be used as such, or in combination with suitable inert, solid materials acting as binding agents. For that purpose, oxide compounds of the type of silica, alumina, and titanium, magnesium and zirconium oxides, either taken as individual compounds or combined with one another, result to be suitable. The catalyst and the binder can be mixed in mutual ratios, by weight, comprised within the range of from 30:70 to 90:10 and preferably of from 50:50 to 70:30. The above said two components can be bonded and compacted in their end desired shape, for example, as extrudates or pellets. According to an alternative route, the silica-alumina gel based catalyst loaded with a noble metal can be prepared by starting from the acidic carrier which already is an extrudate form. In that case, the carrier, as a silica-alumina gel extrudate prepared according to the process disclosed in EP-A-550 922 is impregnated with a suitable aqueous solution of a noble metal compound, then is dried and submitted to thermal treatment according to the same process as disclosed for the acidic carrier in powder form. These steps can be carried out in a similar way also in the case of the ion exchange process.

The catalyst prepared according to the above reported techniques, as such, or bonded with an inert material, is active in the hydroisomerization process, which can be carried out either continuously or batchwise.

The hydroisomerization is advantageously carried out in the presence of hydrogen, at a temperature comprised within the range of from 200 to 540°C, preferably of from 250 to 450°C, and under a pressure comprised within the range of from atmospheric pressure up to 25,000 kPa, preferably of from 4,000 to 10,000 kPa.

The effective catalyst amount, expressed as a percent content, by weight, based on the n-paraffin or mixtures of n-paraffins to be hydroisomerized, is generally comprised within the range of from 0.5 to 30% by weight, preferably of from 1 to 15% by weight.

The following experimental examples are reported in order to better illustrate the present invention.

Example 1

The material used as the acidic carrier in the catalysts claimed herein, is prepared according to as disclosed in EP-A-340 868

Two grams of aluminum isopropoxide is dissolved at room temperature in 68.5 g of an aqueous solution of tetrapropyl ammonium hydroxide (TPA-OH at 13.35% by weight/weight). The solution is heated up to 60°C and then 104.1 g of tetraethyl silicate (TES) is added. The resulting mixture displays the following molar ratios: * $\text{SiO}_2:\text{Al}_2\text{O}_3 = 102$,

* $\text{TPA-OH}:\text{SiO}_2 = 0.09$, and

* $\text{H}_2\text{O}:\text{SiO}_2 = 15$.

By keeping this mixture with stirring at 60°C during 40 minutes, a homogeneous gel is formed which is dried under a flowing air stream at 90°C, and then is calcined at 550°C under a flowing nitrogen stream during 3 hours and subsequently under a flowing air stream during a further 10 hours, still at the same temperature.

An X-ray amorphous silica-alumina gel is obtained in a quantitative yield relatively to the initial charged materials.

The so prepared material is used as an acidic carrier on which platinum is deposited by means of an aqueous impregnation.

More particularly, to 10 g of silica-alumina prepared inside a crystallizer, 12.06 ml of an aqueous solution containing H_2PtCl_6 (0.45% by weight/volume and (0.6 M) HCl is added dropwise, with simultaneously carefully mixing. The reactants are kept into contact with each other for 16 hours, then water is evaporated off during 1 hour at the temperature of 60°C in air and the sample is subsequently dried, during 2 hours, at 150°C, still in air. The calcination is carried out at 500°C for 3 hours under a flowing air stream, with the muffle being heated from 23 to 500°C during a 90 minutes time.

The catalyst characterization data are reported in Table 1.

Example 2

The process is carried out with a carrier as from Example 1, by performing the metal phase deposition step by means of the ion exchange method.

To 10 g of amorphous silica-alumina, 80 ml of an aqueous solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (0.06% of Pt by weight/volume) and some drops of NH_4OH at 35% by weight, such as to alkalinify this suspension at $\text{pH} = 9$, are added. The resulting mixture is kept with stirring at room temperature for 1 hour, then is filtered and the filter cake is washed with water. After a 16-hour drying at 110°C in air, the sample is calcined for 3 hours at 400°C under a flowing air stream, with a temperature increase ramp of from 23 to 400°C during 30 minutes.

The characteristics of the catalyst are reported in following Table 1.

Example 3

A catalyst is prepared by starting from a same carrier as from Example 1, by performing the metal phase deposition step by means of the ion exchange method.

Ten grams of carrier as disclosed in Example 1 is added, with stirring at room temperature, to 1000 ml of demineralized water. 27.23 ml of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ (0.01 M) and some drops of NH_4OH at 35%, such as to increase the suspension pH up to about 6, are added; the resulting mixture is kept with stirring for 3 hours at room temperature. The resulting suspension is filtered, the filter cake is washed with water and is allowed to dry at room temperature. The drying takes place at a temperature of 80°C in air for 3 hours, and the calcination is carried out at 250°C for 3 hours, under a flowing air stream.

The characteristics of this catalyst are reported in Table 1.

Example 4

A catalyst is prepared by starting from a same carrier as from Example 1, by performing the metal phase deposition step by means of the aqueous impregnation method.

A volume of 12.06 ml of an aqueous solution of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ (0.005 M) is added dropwise to 10 g of the same carrier as obtained from Example 1. The subsequent impregnation steps are carried out as in Example 1. The calcination is carried out at 250°C during 3 hours under a flowing air stream with a temperature increase rate of $7^\circ\text{C}/\text{minute}$.

The characteristics of this catalyst are reported in Table 1.

Example 5 (comparison Example)

A reference catalyst is prepared which is constituted by platinum supported on beta zeolite.

Said beta zeolite is prepared under similar conditions to as disclosed in US-A-3,308,069.

An amount of 59.8 g of an aqueous solution at 40% by weight/weight of tetraethylammonium hydroxide (TEA-OH) and 1.9 g of sodium aluminate are added to 58.4 g of demineralized water. The resulting mixture is heated up to about 80°C and is kept with stirring until NaAlO_2 is completely dissolved. The resulting solution is added to 48.7 g of colloidal silica Ludox HS at 40% by weight, such as to yield a molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3 = 28$.

The resulting homogeneous suspension, having $\text{pH} = 14$, is charged to a stainless steel autoclave and is caused to crystallize under hydrothermal conditions in an oven at 150°C during a 10-day time, under static conditions, under the autogenous pressure.

The crystallized product is filtered off, the filter cake is washed, is dried for 1 hour at 120°C , is calcined during 5 hours at 550°C and is turned into its acidic form by exchange with ammonium acetate and subsequent calcination under the above indicated conditions.

The Pt metal phase is deposited on the beta zeolite by aqueous impregnation.

In particular, on 10 g of beta zeolite, 12.06 ml of an aqueous solution containing H_2PtCl_6 (0.45%Pt by weight/volume) and HCl (0.6 M) is added dropwise, with careful mixing. The subsequent impregnation, drying and calcination steps are as disclosed in Example 1.

The characteristics of the resulting catalyst are reported in Table 1, in which " $\text{SiO}_2:\text{Al}_2\text{O}_3$ " indicates the molar ratio of silica to alumina, and "Pore d_m " indicates the average diameter of the pores, expressed as m (Angstrom).

TABLE 1

Cat.	Metal % w/w	Surface area (m ² /g)	SiO ₂ :Al ₂ O ₃ (m/m)	Pore volume (ml/g)	Pore d _m (Å) m
Ex. 1	0.52	674.6	100	0.44	(<30) <30 · 10 ⁻¹⁰
Ex. 2	0.58	496.3	100	0.44	(:30) <30 · 10 ⁻¹⁰
Ex. 3	0.27	485.9	100	0.44	(<30) <30 · 10 ⁻¹⁰
Ex. 4	0.25	590.4	100	0.44	(<30) <30 · 10 ⁻¹⁰
Ex. 5	0.51	626.3	28.3	0.75	(7.5x5.7) 7.5x5.7 · 10 ⁻¹⁰ (6.5x5.6) 6.5x5.6 · 10 ⁻¹⁰

Example 6

The catalyst from Example 1 was tasted in the reaction of hydroisomerization of n-C₁₆ paraffin, in a microautoclave, under the following conditions.

The microautoclave is constituted by a steel body and a cover provided with a plurality of valves for pressurization, venting and optional recovery of gas products, and a pressure relief disk. The stirring system is constituted by a thin internal metal rod.

The reactor is charged with 8 g of C₁₆ paraffin and 0.25 g of catalyst; the system is pressurized when cold with H₂ at 5 MPa and then is heated up to the temperature of 360°C.

As zero time, the point in time is considered when the temperature inside the reactor interior reaches the desired value. After 120 minutes, the reactor is cooled and the internal pressure thereof is relieved, and the reaction mixture is recovered. The analysis of the products in order to determine the conversion and their distribution is directly carried out on the mixture, by gas chromatography (crosslinked methyl silicone gum HP-1 column, atomic emission detector).

In Table 2, the values of conversion and selectivity are reported, which were computed as follows:

$$n\text{-C}_{16} \text{ conversion} = \frac{\text{unreacted } n\text{-C}_{16} \text{ peak surface area}}{\text{total hydrogen peak surface area}}$$

$$\text{selectivity to iso-C}_{16} = \frac{\text{produced iso-C}_{16} \text{ peak surface area}}{\text{total product peak surface area}}$$

$$\text{selectivity to C}_{16^-} = \frac{\text{produced C}_{16^-} \text{ peak surface area}}{\text{total product peak surface area}}$$

in which "iso-C₁₆" is the mixture of isomers containing 16 carbon atoms, and "C₁₆⁻" is the mixture of cracking products, with less than 16 carbon atoms.

Example 7

A catalyst according to Example 2 is tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as in Example 6. The values of conversion and selectivity are reported in Table 2.

Example 8

A catalyst according to Example 3 is tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as in Example 6. The values of conversion and selectivity are reported in Table 2.

Example 9

A catalyst according to Example 2 is tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as in Example 7, except for the reaction time being extended to 240 minutes. The values of conversion and selectivity are reported in Table 2.

TABLE 2

Example	Conversion %	Selectivity to iso-C ₁₆	Selectivity to C ₁₆ ⁻
6 *	79.5	87.29	12.70
7 *	19.0	94.48	5.52
8 *	25.5	96.39	3.61
9 +	26.3	95.67	4.33
Reaction conditions: T = 360°C, P _{H2} = 5 MPa, n-C ₁₆ :catalyst = 8:0.25;			

* time = 120 minutes;

+ time = 240 minutes.

From Examples 6 and 7, one may observe how the metal phase deposition method has an influence on the conversion rate, with the operating conditions being the same. From Examples 8 (Pd containing catalyst) and 9 (Pt containing catalyst), one may observe that the hydrogenating function performed by palladium supplies the system with a slightly better hydroisomerizing performance than with platinum.

The processes described in technical literature for the hydroisomerization of waxes (e.g., EP-A-225 053 and EP-A-321,307) limit the conversion rates to values comprised within the range of from 20 to 40% by weight, in order to keep the cracking byproducts to their minimum; the catalysts from Examples 2 and 3 displayed such catalytic activities, which made it possible the resulting conversion rates to fall within the range taken into consideration, with extremely good selectivity values to iso-C₁₆ products.

Example 10 (comparison Example).

The catalyst taken as the reference catalyst (Example 5) is tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as in Example 6. The conversion rate and selectivity values are reported in Table 3.

Example 11 (comparison Example).

The catalyst taken as the reference catalyst (Example 5) is tested in the hydroisomerization of n-C₂₈ paraffins. The reaction conditions are the same as in Example 6. The conversion rate and selectivity values are reported in Table 3.

Example 12

A catalyst according to Example 1 is tested in the hydroisomerization of n-C₂₈ paraffins. The reaction conditions are the same as in Example 11. The values of conversion rate and selectivity are reported in Table 3.

TABLE 3

Example	Conversion %	Selectivity to iso species	Selectivity to cracked species
6 *	79.5	87.29	12.70
10 *	86.0	13.26	86.74
11 +	98.1	/	100
12 +	61.2	94.12	5.89
Reaction conditions: T = 360°C, t = 120 minutes, P _{H2} = 5 MPa, substrate:catalyst = 8:0.25.			

* substrate = n-C₁₆;+ substrate = n-C₂₈

From the tests of the Examples 6, 10, 11 and 12, it was verified that the catalysts according to the present invention (Examples 6 and 12) display a higher hydroisomerization selectivity, in the hydroisomerization of both n-C₁₆ and n-C₂₈ paraffins, with the operating conditions being the same, as compared to a catalyst taken as the reference catalyst (Examples 10 and 11).

Example 13

A catalyst as from Example 1, is tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are kept equal to those as of Example 6 in order to verify the reproducibility of the process. The values of conversion rate and selectivity are reported in Table 4.

Example 14

A catalyst as from Example 1, is first dried in an N₂ atmosphere at 300°C and is subsequently tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as of Example 6. The values of conversion rate and selectivity are reported in Table 4.

Example 15

A catalyst as from Example 1, is first activated under a H₂ atmosphere at 400°C and is subsequently tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as of Example 6. The values of conversion rate and selectivity are reported in Table 4.

Example 16

A catalyst as from Example 1, is first activated as in Example 15 and is subsequently tested in the hydroisomerization of n-C₁₆ paraffins. The reaction conditions are the same as of Example 15, except for the reaction time, which is reduced down to 60 minutes. The values of conversion and selectivity are reported in Table 4.

TABLE 4

Example	Conversion %	Selectivity to iso-C ₁₆	Selectivity to C ₁₆ *
6	79.5	87.29	12.7
13	79.4	86.52	13.48
14	72.0	89.03	10.97
15	72.2	90.44	9.56
16 *	39.8	89.45	10.55

Reaction conditions:
T = 360°C, T = 120 minutes, P_{H2} = 5 MPa, n-C₁₆:catalyst = 8:0.25;

* t = 60 minutes.

From Examples 6 and 13, the extremely good reproducibility of the reaction system emerges.

From Examples 6, 14 and 15 one may observe that, against a yield decrease of 8% by weight, the selectivity ratio of iso-C₁₆:C₁₆ is favoured by an activating treatment, in particular by a reducing treatment (Example 15).

From Examples 15 and 16, it may be observed that halving the test time actually causes decrease in conversion rate, with the selectivity to iso-C₁₆ products remaining nearly constant.

Claims

1. Bifunctional catalyst for the hydroisomerization of n-paraffins containing more than 15 carbon atoms constituted by:

(a) a carrier of acidic character constituted by a calcined X-ray amorphous silica and alumina gel, with a molar ratio of SiO₂:Al₂O₃ comprised within the range of from 30:1 to 500:1, a surface area comprised within the range of from 500 to 1000 m²/g, with a porosity comprised within the range of from 0.3 to 0.6 ml/g, with an average diameter of pores comprised within the range of from 10 to 30 · 10⁻¹⁰ m (10 to 30 Angstroms);

(b) one or more noble metals belonging to Group VIIIA, in amounts comprised within the range of from 0.05 to 5% by weight.

2. Bifunctional catalyst according to claim 1, characterized in that the acidic carrier displays a ratio of SiO₂:Al₂O₃ comprised within the range of from 50:1 to 300:1 and a porosity of 0.4-0.5 ml/g, and the noble metal, selected from platinum and palladium, is contained at a level of from 0.1 to 2% by weight.

3. Catalyst according to claim 1 or 2, characterized in that it is mixed with suitable inert solid materials performing the task of binding agent.

4. Process for preparing bifunctional catalyst according to claim 1 or 2, characterized in that said process comprises the following steps:

-- bringing the amorphous silica-alumina gel into contact with an aqueous solution of a compound of the noble metal, at room or close-to-room temperatures, and at a pH comprised between 1 and 4;

-- drying the so treated silica-alumina gel;

-- heating said gel in an oxidizing atmosphere at temperatures comprised within the range of from 200 to 600°C.

5. Process for preparing the bifunctional catalyst according to claim 1 or 2, characterized in that said process comprises the following steps:

-- suspending the silica-alumina gel in an aqueous solution of a complex or salt of a noble metal at room or close-to-room temperatures, and at a pH comprised between 6 and 10;

-- separating the solid matter, washing it with water and drying it;

-- submitting the resulting solid matter to a thermal treatment under an inert or oxidizing atmosphere, at temperatures comprised within the range of from 200 to 600°C.

6. Process for preparing the bifunctional catalyst according to claims 4 or 5, characterized in that it comprises a subsequent activation step, carried out by drying and/or reduction.
7. Process for preparing the bifunctional catalyst according to claim 6, characterized in that the activation step comprises a drying stage and a reduction stage.
8. Process for hydroisomerizing n-paraffins containing more than 15 carbon atoms, characterized in that the n-paraffin, or the mixture of n-paraffins, is brought into contact, under hydroisomerization conditions, with the bifunctional catalyst according to claims from 1 to 3.
9. Process for hydroisomerizing n-paraffin according to claim 8, characterized in that said process is carried out in the presence of an amount of bifunctional catalyst comprised within the range of from 0.5 to 30% by weight, based on n-paraffins, at a temperature comprised within the range of from 200 to 540°C, and under a hydrogen pressure comprised within the range of from atmospheric pressure up to 25,000 kPa.
10. Process according to claim 9, characterized in that it is carried out in the presence of a bifunctional catalyst used in an amount comprised within the range of from 1 to 15% by weight based on n-paraffins, at a temperature comprised within the range of from 250 to 450°C, and under a hydrogen pressure comprised within the range of from 4,000 to 10,000 kPa.

Patentansprüche

1. Bifunktionaler Katalysator zur Hydroisomerisierung von n-Paraffinen, enthaltend mehr als 15 Kohlenstoffatome, bestehend aus
 - (a) einen Träger mit saurem Charakter, bestehend aus einem calcinierten röntgenamorphen Kieselsäure- und Tonerdegel mit einem Mol-Verhältnis von $\text{SiO}_2:\text{Al}_2\text{O}_3$ im Bereich von 30:1 bis 500:1, einer Oberfläche im Bereich von 500 bis 1000 m^2/g , mit einer Porosität im Bereich von 0,3 bis 0,6 ml/g , mit einem mittleren Porendurchmesser im Bereich von 10 bis 30 $\times 10^{-10}\text{m}$ (10 bis 30 Ångström);
 - (b) einem oder mehreren Edelmetallen der Gruppe VIIIA, in Mengen im Bereich von 0,05 bis 5 Gew.-%.
2. Bifunktionaler Katalysator nach Anspruch 1, dadurch gekennzeichnet, daß der saure Charakter ein Verhältnis von $\text{SiO}_2 : \text{Al}_2\text{O}_3$ im Bereich von 50 : 1 bis 300 : 1 anzeigt und eine Porosität von 0,4 bis 0,5 ml/g , und das Edelmetall, ausgewählt aus Platin und Palladium, in einer Menge von 0,1 bis 2 Gew.-% enthalten ist.
3. Katalysator nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß er mit geeigneten inerten festen Materialien vermischt ist, die die Aufgabe eines Bindemittels erfüllen.
4. Verfahren zur Herstellung des bifunktionalen Katalysators nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Verfahren die folgenden Stufen umfaßt:
 - In-Kontakt-bringen des amorphen Kieselsäure/Tonerde-Gels mit einer wäßrigen Lösung einer Verbindung des Edelmetalls bei Raumtemperatur oder Temperaturen nahe Raumtemperatur und bei einem pH-Wert zwischen 1 und 4;
 - Trocknen des so behandelten Kieselsäure/Tonerde-Gels;
 - Erhitzen des Gels in einer oxidierenden Atmosphäre bei Temperaturen im Bereich von 200 bis 600°C.
5. Verfahren zur Herstellung des bifunktionalen Katalysators nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Verfahren die folgenden Stufen umfaßt:
 - Suspendieren des Kieselsäure/Tonerde-Gels in einer wäßrigen Lösung eines Komplexes oder Salzes eines Edelmetalls bei Raumtemperatur oder Temperaturen nahe Raumtemperatur und bei einem pH-Wert im Bereich von 6 bis 10;
 - Abtrennen der festen Bestandteile, Waschen mit Wasser und Trocknen;
 - Unterwerfen des erhaltenen festen Materials einer thermischen Behandlung unter einer inerten oder oxidierenden Atmosphäre bei Temperaturen im Bereich von 200 bis 600°C.

6. Verfahren zur Herstellung des bifunktionellen Katalysators nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß es eine anschließende Aktivierungsstufe umfaßt, die durchgeführt wird durch Trocknen und/oder Reduzieren.
7. Verfahren zur Herstellung des bifunktionellen Katalysators nach Anspruch 6, dadurch gekennzeichnet, daß die Aktivierungsstufe eine Trockenstufe und eine Reduktionsstufe umfaßt.
8. Verfahren zum Hydroisomerisieren von n-Paraffinen, enthaltend mehr als 15 Kohlenstoffatome, dadurch gekennzeichnet, daß das n-Paraffin oder das Gemisch von n-Paraffinen unter Hydroisomerisierungsbedingungen mit dem bifunktionellen Katalysator nach den Ansprüchen 1 bis 3 zusammengebracht wird.
9. Verfahren zum Hydroisomerisieren von n-Paraffin nach Anspruch 8, dadurch gekennzeichnet, daß das Verfahren in Gegenwart einer Menge an bifunktionellem Katalysator durchgeführt wird im Bereich von 0,5 bis 30 Gew.-%, bezogen auf n-Paraffine, bei einer Temperatur im Bereich von 200 bis 540°C und unter einem Wasserstoffdruck im Bereich von Atmosphärendruck bis zu 25 000 kPa.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß es in Gegenwart eines bifunktionellen Katalysators in einer Menge im Bereich von 1 bis 15 Gew.-%, bezogen auf n-Paraffine, bei einer Temperatur im Bereich von 250 bis 450°C und unter einem Wasserstoffdruck im Bereich von 4 000 bis 10 000 kPa durchgeführt wird.

20 Revendications

1. Catalyseur bifonctionnel pour l'hydroisomérisation des paraffines normales renfermant plus de 15 atomes de carbone, constitué de :
 - (a) un support de caractère acide, constitué d'un gel de silice et d'alumine, amorphe d'après l'analyse aux rayons X, calciné, présentant un rapport molaire $\text{SiO}_2 : \text{Al}_2\text{O}_3$ compris dans l'intervalle allant de 30:1 à 500:1, une surface spécifique comprise dans l'intervalle allant de 500 à 1000 m^2/g , une porosité comprise dans l'intervalle allant de 0,3 à 0,6 ml/g, et un diamètre moyen des pores compris dans l'intervalle allant de $10 \times 10^{-10}\text{m}$ à $30 \times 10^{-10}\text{m}$ (10 à 30 Angstroms),
 - (b) un ou plusieurs métaux nobles appartenant au groupe VIIIA, présents en une proportion comprise dans l'intervalle allant de 0,05% en poids à 5% en poids.
2. Catalyseur bifonctionnel selon la revendication 1, caractérisé en ce que le support acide présente un rapport $\text{SiO}_2 : \text{Al}_2\text{O}_3$ compris dans l'intervalle allant de 50:1 à 300:1 et une porosité de 0,4 à 0,5 ml/g, et en ce que le métal noble, choisi parmi le platine et le palladium, est présent en une proportion de 0,1% en poids à 2% en poids.
3. Catalyseur selon la revendication 1 ou 2, caractérisé en ce que il est mélangé avec des matières solides inertes appropriées, remplissant le rôle d'agent liant.
4. Procédé de préparation d'un catalyseur bifonctionnel selon la revendication 1 ou 2, caractérisé en ce qu'il comprend les étapes suivantes :
 - mettre le gel amorphe de silice et d'alumine en contact avec une solution aqueuse d'un dérivé du métal noble, en opérant à la température de la salle ou à une température proche de la température de la salle et à un pH compris entre 1 et 4,
 - sécher le gel de silice et d'alumine ainsi traité,
 - chauffer ledit gel dans une atmosphère oxydante, à une température comprise dans l'intervalle allant de 200 à 600°C.
5. Procédé de préparation du catalyseur bifonctionnel selon la revendication 1 ou 2, caractérisé en ce qu'il comprend les étapes suivantes :
 - mettre le gel de silice et d'alumine en suspension dans une solution aqueuse d'un complexe ou d'un sel d'un métal noble, en opérant à la température de la salle ou à une température proche de la température de la salle et à un pH compris entre 6 et 10,
 - séparer la matière solide, la laver avec de l'eau et la sécher,
 - soumettre la matière solide résultante à un traitement thermique dans une atmosphère inerte ou oxydante, à une température comprise dans l'intervalle allant de 200 à 600°C.

6. Procédé de préparation du catalyseur bifonctionnel selon la revendication 4 ou 5, caractérisé en ce qu'il comprend une étape d'activation ultérieure, réalisée par séchage et/ou réduction.
- 5 7. Procédé de préparation du catalyseur bifonctionnel selon la revendication 6, caractérisé en ce que l'étape d'activation comprend une étape de séchage et une étape de réduction.
8. Procédé d'hydroisomérisation des paraffines normales contenant plus de 15 atomes de carbone, caractérisé en ce que l'on met la paraffine normale ou le mélange de paraffines normales en contact avec le catalyseur bifonctionnel selon l'une quelconque des revendications 1 à 3, dans des conditions d'hydroisomérisation.
- 10 9. Procédé d'hydroisomérisation des paraffines normales selon la revendication 8, caractérisé en ce que l'on réalise ledit procédé en présence d'une proportion de catalyseur bifonctionnel comprise dans l'intervalle allant de 0,5 à 30% en poids par rapport aux paraffines normales, à une température comprise dans l'intervalle allant de 200 à 540°C, et sous une pression d'hydrogène comprise dans l'intervalle allant de la pression atmosphérique à 25 000 kPa.
- 15 10. Procédé selon la revendication 9, caractérisé en ce qu'il est réalisé en présence d'un catalyseur bifonctionnel, utilisé en une proportion comprise dans l'intervalle allant de 1 à 15% en poids par rapport aux paraffines normales, à une température comprise dans l'intervalle allant de 250 à 450°C et sous une pression d'hydrogène comprise dans l'intervalle allant de 4000 à 10 000 kPa.
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